



dDNP as an emergent real time analytical method for catalytic reactions

Boeg, Peter Andreas; Mossin, Susanne; Duus, Jens Øllgaard; Ardenkjær-Larsen, Jan Henrik; Karlsson, Magnus

Publication date:
2017

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Boeg, P. A., Mossin, S., Duus, J. Ø., Ardenkjær-Larsen, J. H., & Karlsson, M. (2017). *dDNP as an emergent real time analytical method for catalytic reactions*. Abstract from EUROMAR 2017, Warsaw, Poland.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

dDNP as an emerging real time analytical method for catalytic reactions

Peter Andreas Boeg¹, Susanne Mossin¹, Jens Ø. Duus¹, Jan H. Ardenkjær-Larsen², and Magnus Karlsson²

¹Department of Chemistry, Technical University of Denmark, 2800 Lyngby, Denmark, ²Department of Electrical Engineering, Technical University of Denmark, 2800 Lyngby, Denmark

Dissolution dynamic nuclear polarization NMR (dDNP) hyperpolarization method is used for the investigation of enzymatic and metabolic systems. Improving the signal-to-noise ratio by more than 10,000 compared to conventional NMR, the method significantly expands the applicability and efficiency of conventional NMR¹. We are working to develop this methodology further to include catalytic and inorganic chemistry.

The dedicated instrumentation for hyperpolarization is becoming increasingly versatile for applications within chemistry, biology and medicine and is used to answer scientific questions of a both fundamental and applied nature. By applying dDNP to catalytic science, we are allowing real time monitoring of catalytic reaction mechanisms and intermediates. Understanding the direct correlation between the structure of the catalyst and the selectivity of the reaction remains a great challenge in most of catalysis, and facilitate the continued improvement and development of new catalysts.

A target reaction of the project has been the hydrogenation of simple alkenes and alkene esters using Shrock-Osborn, Crabtree and Wilkinson's catalysts. Hydrogenation of olefins are relevant for both industrial and research applications.

We report here the results of following the hydrogenation reactions with dDNP. The suitability of various solvents and substrates, the requirements on the reaction speed and the reaction conditions have been assessed for dDNP conditions.

The potential of the method towards obtaining kinetic and mechanistic insights by time-resolved dDNP is illustrated in Figures 1 and 2. It is shown how Rh(NBD)(DPPB), a Shrock-Osborn catalyst, competitively catalyses the hydrogenation of two similar unlabeled alkene esters. The reaction has been followed with a time resolution of 2 seconds over a range of 2 minutes. It is seen how different reaction rates are observed despite equal initial substrate concentrations. The substrate with the terminal alkene reacts faster than the conjugated alkene as would be expected. The catalyst activity has been calculated from evolution of the peak intensities.

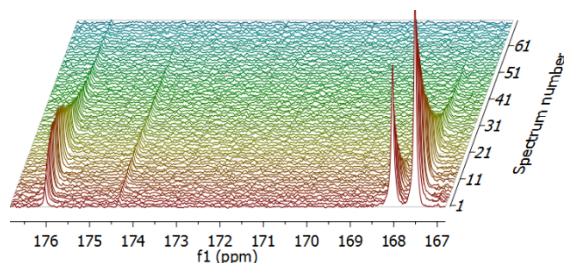


Fig. 1 Hydrogenation of butyl acrylate and trans-methyl crotonate over Rh(NBD)(DPPB), a Shrock-Osborn catalyst. The stacked ¹³C-NMR spectra (carbonyl range of the spectra) show the time-resolved development of the system over 2 minutes. Substrate peaks are found to the right and product peaks to the left.

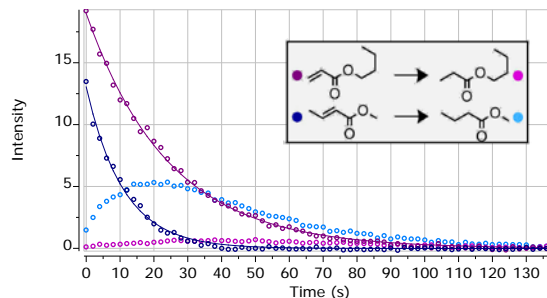


Fig. 2 Time-resolved intensities of the substrate and product carbonyl peaks in Figure 1.

Slight variations in the reaction conditions provide valuable insight into the workings of the system including substrate inhibition, rate limiting factors, kinetic isotope effects and mechanistic information. ¹³C-labelling substrates will potentially allow for full mechanistic elucidation and observation of intermediates.

Acknowledgments

We thank the Danish National Research Foundation (DNRF124) for funding the HYPERMAG Centre of Excellence.

¹ J. H. Ardenkjær-Larsen et al., Increase in signal-to-noise ratio of > 10,000 times in liquid-state NMR, Proc. Natl. Acad. Sci. U. S., 100, 10158–10163, 2003.